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Electro-oxidation of Diarylacetylenes and Diaryldiacetylenes

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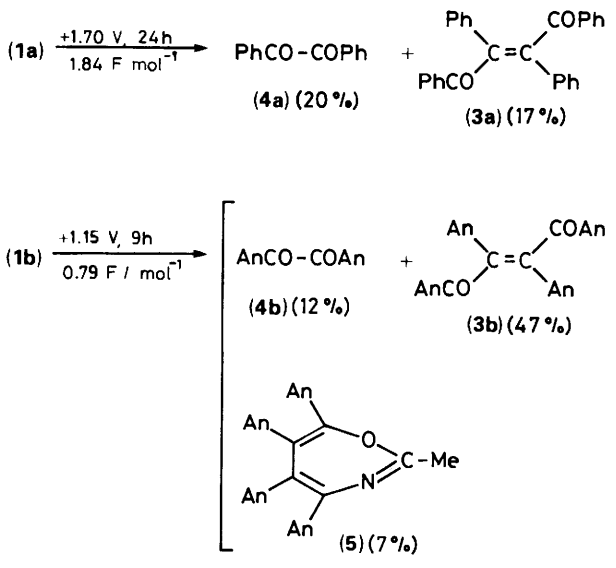
Diarylacetylenes led to 1,2-diaroyl-1,2-diarylethylenes and diaryldiacetylenes led to a mixture of acetylenic α- and γ-diketones, by anodic oxidation in MeCN–$LiClO_4$ on a graphite plate electrode.

Until now, the anodic oxidation of diphenylacetylene has only been carried out in solvent–electrolyte systems (AcOH–AcONa,[1] MeOH–NaCN,[2] MeOH–$LiClO_4$[3]) where the electrogenerated cation radical reacts either with the solvent (MeOH) or with the electrolyte anion (AcO^-, NC^-).

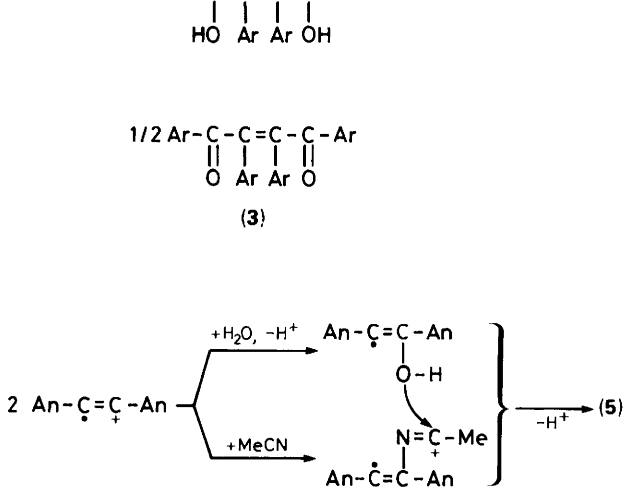
On the other hand, recently, it was reported[4] that the photochemical oxidation of diphenylacetylene gave 1,2,3-triphenylazulene. This dimerisation, postulated to occur *via* the cation radical, suggested that azulenes might be formed by electro-oxidation of diarylacetylenes in MeCN–$LiClO_4$.

Here we report our results on the anodic behaviour of diarylacetylenes (Ar–C≡C–Ar) (**1**) and conjugated diaryldiacetylenes (Ar–C≡C–C≡C–Ar) (**2**) (**a**, Ar = Ph; **b**, Ar = *p*-$MeOC_6H_4$ = An) for comparison of results. At a platinum microanode these substrates undergo irreversible oxidation steps located at 1.64 (**1a**), 1.17 (**1b**); 1.84 (**2a**), and 1.35 V (**2b**) (electrolyte: 0.1 M MeCN–$LiClO_4$, reference: saturated calomel electrode, scan rate: 100 mV s^{-1}).

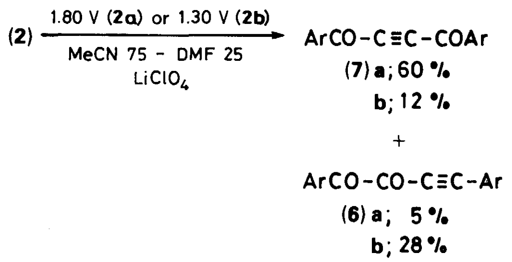
Macro-scale electrolyses were carried out in 0.3 M MeCN–$LiClO_4$ (giving better results than CH_2Cl_2–Bu_4NBF_4), using a graphite plate anode (A = 10 cm^2) [such an anode material was essential to overcome the very high passivation observed at smooth-surfaced electrodes (platinum or glassy carbon)] and a graphite rod cathode, in a divided H-cell. Electrolyses were always conducted in the absence of soluble base



Scheme 1



Scheme 2



Scheme 3

(2,6-lutidine) or insoluble base (K_2CO_3) which gave tars (even though, in most cases, the acidity generated at an anode is responsible for the decomposition of products). In the anode compartment (60 ml) acetylenes (**1**) or (**2**) (4 mmol) were added.

In the case of diarylacetylenes (**1**), the expected 1,2,3-triarylazulenes were not formed; among the electrolysis products, were isolated 1,2-diaroyl-1,2-diarylethylenes (**3**) together with benzils (**4**); (**1b**) gave also oxazepine (**5**) (Scheme 1). The proposed mechanism for the formation of diaroylstilbenes (**3**) involves the reaction of the residual water on cation radical of (**1**) [so, is formed an enol radical dimerizing in a di-enol readily oxidisable into a dication losing two protons to lead to (**3**)], and for oxazepine (**5**) the addition of acetonitrile on this cation radical must also be considered (Scheme 2). The absence of azulene product is probably due to the instability of its cation radical (if formed) giving only degradation reactions.

In the case of diaryldiacetylenes (**2**), a mixture of acetylenic α-diketone (**6**) and acetylenic γ-diketone (**7**) was obtained (Scheme 3); yields were improved by the addition of 25% dimethylformamide (DMF) to MeCN. The mechanism also involves an attack of the cation radical by the residual water whose average concentration was estimated at about 1000 p.p.m.

It is worth mentioning that electro-oxidation of 1,4-diphenylbutadiyne (**2a**) into dibenzoylacetylene PhCO–C≡C–COPh (**7a**) with a 60% yield, appears to be a good synthesis of this interesting dienophile.[5] Moreover, one should note the electrosynthesis of acetylenic α-diketones (**6**) which would be difficult to prepare by means of conventional methods.

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